

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-238855

(43)Date of publication of application : 17.09.1993

---

(51)Int.Cl.

C04B 41/87

C04B 41/80

---

(21)Application number : 04-043578

(71)Applicant : TOKYO ELECTRIC POWER CO  
INC:THE  
NGK INSULATORS LTD

(22)Date of filing : 28.02.1992

(72)Inventor : FURUSE YUTAKA  
ENDO YASUYUKI  
TAKAHASHI TOMONORI  
KOBAYASHI HIROMICHI

---

## (54) PRODUCTION OF CERAMIC COATING MEMBER

### (57)Abstract:

**PURPOSE:** To provide a method of producing a ceramic coating member having good adhesion between a ceramic substrate and the coating layer, excellent high-temperature strength and heat resistance and good oxidation resistance and corrosion resistance and high in reliability.

**CONSTITUTION:** The surface of a ceramic substrate consisting of a material selected from silicon carbide, silicon nitride or a silicon carbide-dispersed and strengthened silicon nitride composite material is subjected to mechanical processing, heat-treatment or chemical treatment so that ten point average roughness (Rz) as surface roughness may be  $\geq 1.5\mu\text{m}$  and average roughness of center line (Ra) may be  $\geq 0.2\mu\text{m}$  and then at least one kind of material selected from alumina, mullite, zircon, zirconia and yttria is subjected to plasma spray coating onto the surface of the substrate so as to give  $\geq 50\mu\text{m}$  thickness of a ceramic coating layer to provide the objective ceramic coating member.

---

## LEGAL STATUS

[Date of request for examination] 27.11.1998

[Date of sending the examiner's decision of rejection] 15.02.2001

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] The ingredient of a base material is chosen from silicon carbide, silicon nitride, or silicon carbide dispersion-strengthening silicon nitride composite. The ten-point average of roughness height (notation Rz) machines the front face of a base material as surface roughness to extent from which 1.5 micrometers or more and the center line average of roughness height (notation Ra) are set to 0.2 micrometers or more. The manufacture approach of the ceramic-coating member characterized by carrying out chemical preparation and carrying out the plasma metal spray of heat treatment or at least one or more sorts which are chosen from an alumina, a mullite, zircon, a zirconia, and yttria subsequently to the front face of a base material.

[Claim 2] The manufacture approach of the ceramic-coating member according to claim 1 characterized by setting to 50 micrometers or more thickness of the ceramic-coating layer obtained by said plasma metal spray.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. \*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

**[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the manufacture approach of a ceramic-coating member.

**[0002]**

**[Description of the Prior Art]** Conventionally, as an elevated-temperature structural material used under a severe condition at an elevated temperature, ceramic ingredients, such as silicon carbide and silicon nitride, are known.

**[0003]**

**[Problem(s) to be Solved by the Invention]** However, also although it is called elevated-temperature heat-resisting material, such as such silicon carbide or silicon nitride, if exposed to the combustion gas in which these ingredients have the high-speed rate of flow, high temperature oxidation, high temperature corrosion, etc. will thin down a member in many cases. For this reason, in order to improve endurance about the member exposed to combustion gas with the high-speed rate of flow, it is the biggest technical problem to raise oxidation resistance.

**[0004]** Although the approach of carrying out surface coating of the oxide ceramics to the base material front face of elevated-temperature heat-resisting material for this technical-problem solution is proposed, even if it cannot cover oxide ceramics with the surface state of a base material or can cover, according to this approach, it may exfoliate by use in an elevated temperature for a short time. The adhesion of a ceramic base material and an enveloping layer becomes good, the purpose of this invention is excellent in high temperature strength and thermal resistance, and oxidation resistance and corrosion resistance are to offer the manufacture approach of a good reliable ceramic-coating member.

**[0005]**

**[Means for Solving the Problem]** The manufacture approach of the ceramic-coating member by this invention for attaining said purpose The ingredient of a base material is chosen from silicon carbide, silicon nitride, or silicon carbide dispersion-strengthening silicon nitride composite. The ten-point average of roughness height (notation Rz) machines the front face of a base material as surface roughness to extent from which 1.5 micrometers or more and the center line average of roughness height (notation Ra) are set to 0.2 micrometers or more. It is characterized by carrying out chemical preparation and carrying out the plasma metal spray of heat treatment or at least one or more sorts which are chosen from an alumina, a mullite, zircon, a zirconia, and yttria subsequently to the front face of a base material.

**[0006]** It is because it becomes difficult for that set said ten-point average of roughness height (notation Rz) to 1.5 micrometers or more, and under these values set said center line average of roughness height (notation Ra) to 0.2 micrometers or more to cover an alumina, a mullite, zircon, a zirconia, or yttria with sufficient endurance firmly on the surface of a base material. As for the thickness of the ceramic-coating layer obtained by said plasma metal spray, it is desirable to be referred to as 50 micrometers or more. Thickness of said ceramic-coating layer was set to 50 micrometers or more under a severe service

condition which contacts high-speed combustion gas etc. because a problem was in dependability [ in / that the thickness of said ceramic-coating layer is less than 50 micrometers / prolonged use ].

[0007]

[Function] Since according to the manufacture approach of the ceramic-coating member of this invention the front face of the ceramic base material before coating is made into proper field granularity and the enveloping layer by the plasma metal spray is formed in this base material front face by which surface roughening was carried out, the adhesion of a ceramic base material and a cladding material becomes good, and a reliable ceramic-coating member can be manufactured.

[0008]

[Example] Hereafter, the example of this invention is explained. The silicon carbide sintered compact which uses B<sub>4</sub>C and C as an additive (examples 1-5, examples 1-5 of a comparison), Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> The silicon nitride sintered compact used as an additive (examples 6-10, examples 6-10 of a comparison), And Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> The compound sintered compact (examples 11-15, examples 11-15 of a comparison) which used as the base material the silicon nitride used as an additive, and added the silicon carbide particle or the whisker as reinforcement was used for the base material, and it investigated about the adhesion of base material surface roughness and an oxide enveloping layer. A test piece configuration is 40mm in width of face of 4mm, height of 3mm, and die length.

[0009] It is shown in the following table 1 for details.

[0010]

[Table 1]

区分	基材	基材の表面粗さ (μm)		溶射材	被覆層の付着状態	耐熱サイクルによる密着性
		Rz	Ra			
実施例 1	炭化珪素	1.7	0.2	アルミナ	良好	良好
実施例 2	炭化珪素	1.7	0.2	ムライト	良好	良好
実施例 3	炭化珪素	1.7	0.2	ジルコン	良好	良好
実施例 4	炭化珪素	1.7	0.2	ジルコニア	良好	良好
実施例 5	炭化珪素	1.7	0.2	イットリア	良好	良好
実施例 6	窒化珪素	1.6	0.2	アルミナ	良好	良好
実施例 7	窒化珪素	1.6	0.2	ムライト	良好	良好
実施例 8	窒化珪素	1.6	0.2	ジルコン	良好	良好
実施例 9	窒化珪素	1.6	0.2	ジルコニア	良好	良好
実施例 10	窒化珪素	1.6	0.2	イットリア	良好	良好
実施例 11	複合材	12.0	2.2	アルミナ	良好	良好
実施例 12	複合材	12.0	2.2	ムライト	良好	良好
実施例 13	複合材	12.0	2.2	ジルコン	良好	良好
実施例 14	複合材	12.0	2.2	ジルコニア	良好	良好
実施例 15	複合材	12.0	2.2	イットリア	良好	良好
比較例 1	炭化珪素	0.7	0.1	アルミナ	不良	—
比較例 2	炭化珪素	0.7	0.1	ムライト	不良	—
比較例 3	炭化珪素	0.7	0.1	ジルコン	不良	—
比較例 4	炭化珪素	0.7	0.1	ジルコニア	不良	—
比較例 5	炭化珪素	0.7	0.1	イットリア	不良	—
比較例 6	窒化珪素	1.1	0.1	アルミナ	良好	不良 (剥離性)
比較例 7	窒化珪素	1.1	0.1	ムライト	良好	不良 (剥離性)
比較例 8	窒化珪素	1.1	0.1	ジルコン	良好	不良 (剥離性)
比較例 9	窒化珪素	1.1	0.1	ジルコニア	良好	不良 (剥離性)
比較例 10	窒化珪素	1.1	0.1	イットリア	良好	不良 (剥離性)
比較例 11	複合材	1.1	0.1	アルミナ	良好	不良 (剥離性)
比較例 12	複合材	1.1	0.1	ムライト	良好	不良 (剥離性)
比較例 13	複合材	1.1	0.1	ジルコン	良好	不良 (剥離性)
比較例 14	複合材	1.1	0.1	ジルコニア	良好	不良 (剥離性)
比較例 15	複合材	1.1	0.1	イットリア	良好	不良 (剥離性)

Examples 1-5 performed heat treatment of 10 hours at the temperature of 1400 degrees C among atmospheric air among Table 1. Examples 6-10 performed etching processing in 70-degree C HF for 1 hour. Examples 11-15 performed sandblasting processing with the mixed abrasive grain (#36 silicon-carbide abrasive grain 50wt% and #36 alumina abrasive grain 50wt%).

[0011] The base material of the examples 1-5 of a comparison is the processing side which machined the baking side by #140 diamond wheel with silicon carbide. The base material of the examples 6-10 of a comparison performed after processing and the inside of atmospheric air with silicon nitride, and performed heat treatment at the temperature of 1300 degrees C for 1 hour. The base material of the examples 11-15 of a comparison performed after processing and the inside of atmospheric air with composite, and performed heat treatment at the temperature of 1300 degrees C for 1 hour. It formed in the base material of said examples 1-15 and the examples 1-15 of a comparison by the plasma metal spray so that it might become the thickness whose oxide enveloping layer of an alumina, a mullite, zircon, a zirconia, and yttria is about 100 micrometers. Measurement evaluation of the adhesion condition of an oxide enveloping layer and room temperature which were formed of the plasma metal spray, and the heat-resistant cycle property by heating for 1400 degrees C and the repeat of cooling was carried out. The result is as being shown in Table 1.

[0012] \*\* Covering test (oxide covering condition evaluation)

In Table 1, as for the adhesion condition of an enveloping layer, the oxide enveloping layer evaluated by viewing whether it would be covered by homogeneity on the surface of the base material. Consequently, about examples 1-15 and the examples 6-15 of a comparison, the adhesion condition of an oxide enveloping layer was good. About the examples 1-5 of a comparison, covering only by the oxide enveloping layer having only adhered to some base materials was impossible. When the surface roughness of a base material was fine, it became clear that it is difficult to cover an oxide.

[0013] \*\* Load test (heat-resistant cycle evaluation)

The adhesion of a base material and oxide covering performed the heat-resistant cycle by heating between a room temperature and 1400 degrees C, and the repeat of cooling, and observed the base material and the enveloping layer interface with the optical microscope for every one cycle.

Consequently, in a base material and an enveloping layer interface, as for examples 1-15, exfoliation did not produce the repeat of 20 heating between a room temperature and 1400 degrees C, and cooling, either. Exfoliation produced the examples 6-15 of a comparison in the base material and the enveloping layer interface in the repeat of one heating between a room temperature and 1400 degrees C, and cooling. When the surface roughness of a base material was not proper surface roughness, it became clear [ that a heat-resistant cycle cannot be borne ].

[0014]

[Effect of the Invention] As explained above, according to the manufacture approach of the ceramic-coating member of this invention In order to form at least one or more sorts of enveloping layers which make the front face of a ceramic base material proper field granularity, and are chosen from an alumina, a mullite, zircon, a zirconia, and yttria by the plasma metal spray on the surface of a base material, Since the adhesion and the heat-resistant cycle property of a ceramic base material and an oxide enveloping layer become good, it fully bears at an elevated temperature and is effective in the oxidizing quality in an elevated temperature and corrosive being good, and being able to manufacture a reliable ceramic-coating member.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

[Industrial Application] This invention relates to the manufacture approach of a ceramic-coating member.

---

[Translation done.]



**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] As explained above, according to the manufacture approach of the ceramic-coating member of this invention In order to form at least one or more sorts of enveloping layers which make the front face of a ceramic base material proper field granularity, and are chosen from an alumina, a mullite, zircon, a zirconia, and yttria by the plasma metal spray on the surface of a base material, Since the adhesion and the heat-resistant cycle property of a ceramic base material and an oxide enveloping layer become good, it fully bears at an elevated temperature and is effective in the oxidizing quality in an elevated temperature and corrosive being good, and being able to manufacture a reliable ceramic-coating member.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Problem(s) to be Solved by the Invention] However, also although it is called elevated-temperature heat-resisting material, such as such silicon carbide or silicon nitride, if exposed to the combustion gas in which these ingredients have the high-speed rate of flow, high temperature oxidation, high temperature corrosion, etc. will thin down a member in many cases. For this reason, in order to improve endurance about the member exposed to combustion gas with the high-speed rate of flow, it is the biggest technical problem to raise oxidation resistance.

[0004] Although the approach of carrying out surface coating of the oxide ceramics to the base material front face of elevated-temperature heat-resisting material for this technical-problem solution is proposed, even if it cannot cover oxide ceramics with the surface state of a base material or can cover, according to this approach, it may exfoliate by use in an elevated temperature for a short time. The adhesion of a ceramic base material and an enveloping layer becomes good, the purpose of this invention is excellent in high temperature strength and thermal resistance, and oxidation resistance and corrosion resistance are to offer the manufacture approach of a good reliable ceramic-coating member.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**OPERATION**

---

[Function] Since according to the manufacture approach of the ceramic-coating member of this invention the front face of the ceramic base material before coating is made into proper field granularity and the enveloping layer by the plasma metal spray is formed in this base material front face by which surface roughening was carried out, the adhesion of a ceramic base material and a cladding material becomes good, and a reliable ceramic-coating member can be manufactured.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**EXAMPLE**

---

[Example] Hereafter, the example of this invention is explained. The silicon carbide sintered compact which uses B<sub>4</sub>C and C as an additive (examples 1-5, examples 1-5 of a comparison), Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> The silicon nitride sintered compact used as an additive (examples 6-10, examples 6-10 of a comparison), And Y<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> The compound sintered compact (examples 11-15, examples 11-15 of a comparison) which used as the base material the silicon nitride used as an additive, and added the silicon carbide particle or the whisker as reinforcement was used for the base material, and it investigated about the adhesion of base material surface roughness and an oxide enveloping layer. A test piece configuration is 40mm in width of face of 4mm, height of 3mm, and die length.

[0009] It is shown in the following table 1 for details.

[0010]

[Table 1]

区分	基材	基材の表面粗さ (μm)		溶射材	被覆層の付着状態	耐熱サイクルによる密着性
		Rz	Ra			
実施例 1	炭化珪素	1.7	0.2	アルミナ	良好	良好
実施例 2	炭化珪素	1.7	0.2	ムライト	良好	良好
実施例 3	炭化珪素	1.7	0.2	ジルコン	良好	良好
実施例 4	炭化珪素	1.7	0.2	ジルコニア	良好	良好
実施例 5	炭化珪素	1.7	0.2	イットリア	良好	良好
実施例 6	窒化珪素	1.6	0.2	アルミナ	良好	良好
実施例 7	窒化珪素	1.6	0.2	ムライト	良好	良好
実施例 8	窒化珪素	1.6	0.2	ジルコン	良好	良好
実施例 9	窒化珪素	1.6	0.2	ジルコニア	良好	良好
実施例 10	窒化珪素	1.6	0.2	イットリア	良好	良好
実施例 11	複合材	12.0	2.2	アルミナ	良好	良好
実施例 12	複合材	12.0	2.2	ムライト	良好	良好
実施例 13	複合材	12.0	2.2	ジルコン	良好	良好
実施例 14	複合材	12.0	2.2	ジルコニア	良好	良好
実施例 15	複合材	12.0	2.2	イットリア	良好	良好
比較例 1	炭化珪素	0.7	0.1	アルミナ	不良	—
比較例 2	炭化珪素	0.7	0.1	ムライト	不良	—
比較例 3	炭化珪素	0.7	0.1	ジルコン	不良	—
比較例 4	炭化珪素	0.7	0.1	ジルコニア	不良	—
比較例 5	炭化珪素	0.7	0.1	イットリア	不良	—
比較例 6	窒化珪素	1.1	0.1	アルミナ	良好	不良 (剥離)
比較例 7	窒化珪素	1.1	0.1	ムライト	良好	不良 (剥離)
比較例 8	窒化珪素	1.1	0.1	ジルコン	良好	不良 (剥離)
比較例 9	窒化珪素	1.1	0.1	ジルコニア	良好	不良 (剥離)
比較例 10	窒化珪素	1.1	0.1	イットリア	良好	不良 (剥離)
比較例 11	複合材	1.1	0.1	アルミナ	良好	不良 (剥離)
比較例 12	複合材	1.1	0.1	ムライト	良好	不良 (剥離)
比較例 13	複合材	1.1	0.1	ジルコン	良好	不良 (剥離)
比較例 14	複合材	1.1	0.1	ジルコニア	良好	不良 (剥離)
比較例 15	複合材	1.1	0.1	イットリア	良好	不良 (剥離)

Examples 1-5 performed heat treatment of 10 hours at the temperature of 1400 degrees C among atmospheric air among Table 1. Examples 6-10 performed etching processing in 70-degree C HF for 1 hour. Examples 11-15 performed sandblasting processing with the mixed abrasive grain (#36 silicon-carbide abrasive grain 50wt% and #36 alumina abrasive grain 50wt%).

[0011] The base material of the examples 1-5 of a comparison is the processing side which machined the baking side by #140 diamond wheel with silicon carbide. The base material of the examples 6-10 of a comparison performed after processing and the inside of atmospheric air with silicon nitride, and performed heat treatment at the temperature of 1300 degrees C for 1 hour. The base material of the examples 11-15 of a comparison performed after processing and the inside of atmospheric air with composite, and performed heat treatment at the temperature of 1300 degrees C for 1 hour. It formed in the base material of said examples 1-15 and the examples 1-15 of a comparison by the plasma metal spray so that it might become the thickness whose oxide enveloping layer of an alumina, a mullite, zircon, a zirconia, and yttria is about 100 micrometers. Measurement evaluation of the adhesion condition of an oxide enveloping layer and room temperature which were formed of the plasma metal spray, and the heat-resistant cycle property by heating for 1400 degrees C and the repeat of cooling was carried out. The result is as being shown in Table 1.

[0012] \*\* Covering test (oxide covering condition evaluation)

In Table 1, as for the adhesion condition of an enveloping layer, the oxide enveloping layer evaluated by viewing whether it would be covered by homogeneity on the surface of the base material. Consequently, about examples 1-15 and the examples 6-15 of a comparison, the adhesion condition of an oxide enveloping layer was good. About the examples 1-5 of a comparison, covering only by the oxide enveloping layer having only adhered to some base materials was impossible. When the surface roughness of a base material was fine, it became clear that it is difficult to cover an oxide.

[0013] \*\* Load test (heat-resistant cycle evaluation)

The adhesion of a base material and oxide covering performed the heat-resistant cycle by heating between a room temperature and 1400 degrees C, and the repeat of cooling, and observed the base material and the enveloping layer interface with the optical microscope for every one cycle.

Consequently, in a base material and an enveloping layer interface, as for examples 1-15, exfoliation did not produce the repeat of 20 heating between a room temperature and 1400 degrees C, and cooling, either. Exfoliation produced the examples 6-15 of a comparison in the base material and the enveloping layer interface in the repeat of one heating between a room temperature and 1400 degrees C, and cooling. When the surface roughness of a base material was not proper surface roughness, it became clear [ that a heat-resistant cycle cannot be borne ].

[0014]

---

[Translation done.]